## Chapter 12

# Variability in Ocean Color Associated with Phytoplankton and Terrigenous Matter: Time Series Measurements and Algorithm Development at the FRONT Site on the New England Continental Shelf.

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## 12.1 INTRODUCTION

Fronts in the coastal ocean describe areas of strong horizontal gradients in both physical and biological properties associated with tidal mixing and freshwater estuarine output (e.g. Simpson, 1981 and O'Donnell, 1993). Related gradients in optically important constituents mean that fronts can be observed from space as changes in ocean color as well as sea surface temperature (e.g., Dupouy et al., 1986). This research program is designed to determine which processes and optically important constituents must be considered to explain ocean color variations associated with coastal fronts on the New England continental shelf, in particular the National Ocean Partnership Program (NOPP) Front Resolving Observational Network with Telemetry (FRONT) site. This site is located at the mouth of Long Island sound and was selected after the analysis of 12 years of AVHRR data showed the region to be an area of strong frontal activity (Ullman and Cornillon, 1999). FRONT consists of a network of modem nodes that link bottom mounted Acoustic Doppler Current Profilers (ADCPs) and profiling arrays. At the center of the network is the Autonomous Vertically Profiling Plankton Observatory (AVPPO) (Thwaites et al. 1998). The AVPPO consists of buoyant sampling vehicle and a trawl-resistant bottom-mounted enclosure, which holds a winch, the vehicle (when not sampling), batteries, and controller. Three sampling systems are present on the vehicle, a video plankton recorder, a CTD with accessory sensors, and a suite of bio-optical sensors including Satlantic OCI-200 and OCR-200 spectral radiometers and a WetLabs ac-9 dual path absorption and attenuation meter. At preprogrammed times the vehicle is released, floats to the surface, and is then winched back into the enclosure with power and data connection maintained through the winch cable. Communication to shore is possible through a bottom cable and nearby surface telemetry buoy, equipped with a mobile modem, giving the capability for near-real time data transmission and interactive sampling control.

#### 12.2 RESEARCH ACTIVITIES

AVPPO deployments

The AVPPO was deployed during 2003 at the Martha's Vineyard Coastal Observatory (MVCO) as part of the Coastal Carbon Time-series (CCTS, J. Campbell and D. Vandemark – PIs) project of the Coastal Ocean Observation and Analysis (COOA) center of the University of New Hampshire (UNH). The Martha's Vineyard Coast Observatory, which came on-line in June 2001, was designed as a highly flexible facility to provide investigators, from school students to scientists, the means to collect long-term environmental data. It is located off the south shore of the island Martha's Vineyard on the northeastern seaboard of the U.S. between the highly productive waters of the Gulf of Maine (GOM) and the Mid Atlantic Bight (O'Reilly et al. 1987). The cabled facility provides power and communications at an underwater node and at the Air Sea Interaction Tower (ASIT), which is 3 km offshore in 15 m of water. Fast Ethernet communications and large power supply facilitates high bandwidth realtime sampling which

is not possible in moorings traditionally used for coastal measurements. The AVPPO was reconfigured to take advantage of the MVCO infrastructure with power and telemetry obtained from the ASIT and deployed on

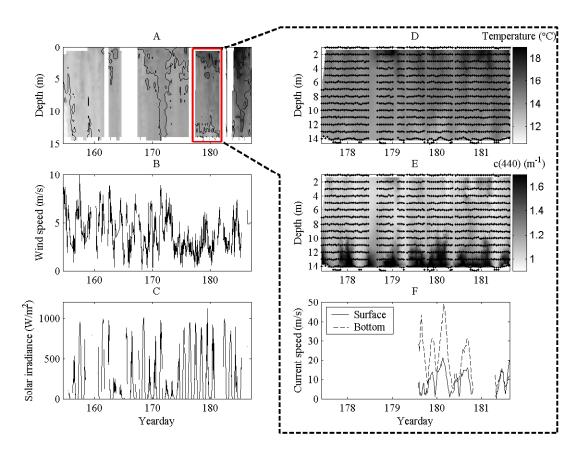


Figure 12.1: Processes at MVCO from AVPPO measurements between 4 June and 8 July 2003. A) The onset of thermal stratification as indicated by interpolated temperature values. High wind (B) events apparently mixed the water column. Stratification intensified with high solar irradiance (C) and low winds after day 172. Expansion of the data between Day 179 and 182 (D-F) shows warm water intrusions at tidal frequencies together with particulate resuspension events (beam attenuation coefficient at 440 nm). Resuspension appears correlated with periods of strong bottom current speeds.

May, 30 2003 at 41 19.412 °N, 70 33.954 °W in approximately 15 m of water. Realtime processing of data was implemented and contour plots are automatically updated at the AVPPO website (http:///4dgeo.whoi.edu/vpr).

#### 12.3 RESEARCH RESULTS

Ongoing observations from the AVPPO illustrate some of the important forcing on the coastal ocean around MVCO. Vertical temperature profiles clearly illustrate warming and the onset of summer stratification modified by mixing induced by surface winds (Fig. 12.1). Initial analysis of beam attenuation coefficient, c ( $\lambda$ ), measured from the AVPPO during this time period also illustrated the effects of tidal forcing. Tidal currents resuspended bottom sediment and appeared to advect differing water masses over the study sight (Fig. 12.1). On maintenance cruises these fronts were clearly visible as distinct lines of surface debris. Wind driven resuspension of sediment is also an important process in coastal oceans and has been observed in previous deployments of the AVPPO in New England coastal waters (Morrison and Sosik 2002a) and in deeper waters south of Martha's Vineyard (Chang 2001).

Using solar stimulated fluorescence (SSF) Morrison (2003) presented evidence of three types of quenching in natural phytoplankton populations, 1) photochemical quenching, 2) rapidly varying energy dependent quenching, qE, of which the xanthophyll cycle is an example (Demmig-Adams and Adams 1992), and 3) quenching associated with photoinhibition, qI, with longer relaxation timescales (Horton et al. 1996). The last two are examples of non-photochemical quenching.

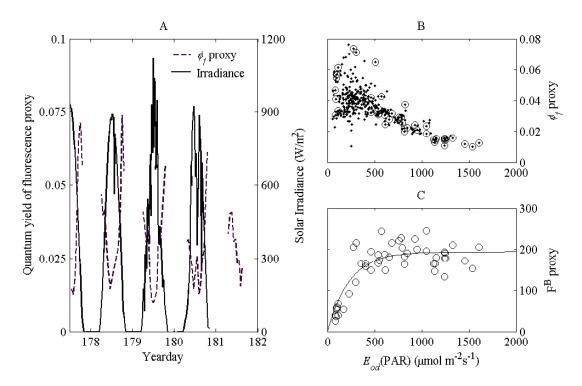


Figure 12.2: Quantum yield of fluorescence proxy from the 25 June – 1 July, 2003. A) Surface φf values demonstrated non-photochemcial quenching decreasing φf during the majority of daytime. Day 180 clearly shows this modulated by surface irradiance. B) Decreases in φf at low irradiances were indicative of photochemical quenching (blue – all depths, red – surface data from A). C) Biomass normalized fluoresce – irradiance showed similar relationships to those reported previously (e.g., Schallenberg et al. 2002)

Similar trends were also observed at MVCO during the summer of 2003. Proxy values of the quantum yield of fluorescence (upwelling radiance at 665 nm used to correct for back- and Raman scattered light) were calculated from radiometric measurements from the AVPPO with the formulations of Morrison (2003, phytoplankton absorption was obtained from ac-9 measurements). The fluorescence yield was suppressed at high irradiances in the middle of the day and responded to varying irradiance conditions induced by clouds (Fig. 12.2A). The transition from photochemically to non-photochemically dominated quenching was apparent both at fixed depths and throughout the water column (Fig. 12.2A and B). To our knowledge, these observations represent one of the most detailed studies of the diurnal variability of the fluorescence yield of natural phytoplankton populations to date.

We have shown previously that absorption spectra measured with an ac-9 can be decomposed into that from phytoplankton and non-algal material (Morrison and Sosik 2002a). This was achieved by assigning characteristic spectral shapes to each fraction and iteratively varying constituent concentrations to minimize the sum of square deviations between observed and predicted spectra. The spectral slope of non-algal material, S, was also iteratively varied to account for different spectral shapes but the phytoplankton absorption shape remained constant. Ciotti et al. (2002) described the phytoplankton absorption shape as a mixing series between two normalized spectra representative of pico- and micro-phytoplankton or minimal and maximal packaging,  $\hat{a}_{ph}^{pico}(\lambda)$  and  $\hat{a}_{ph}^{micro}(\lambda)$ , respectively. Greater than 80% of the variability in the spectral shape of phytoplankton was explained using this method. This parameterization of the phytoplankton absorption shape was included in the previous absorption model and used in the

decomposition. To test the ability of the method to accurately reproduce spectral variation 478 groups of absorption spectra of particles, non-algal particles, and colored dissolved organic material  $(a_p(\lambda), a_{NAP}(\lambda),$  and  $a_{CDOM}(\lambda)$ , respectively) from the North East Atlantic were used to assess the absorption decomposition methods (Morrison and Sosik in prep). Phytoplankton absorption,  $a_{ph}(\lambda)$ , was calculated as the difference between  $a_p(\lambda)$  and  $a_{NAP}(\lambda)$ . Spectra were measured with bench-top spectrophotometers either by ourselves or as part of the Bermuda Bio-Optics Project (Siegel et al. 1995) using standard protocols (Mitchell et al. 2000) and are archived at the NASA Seabass database.

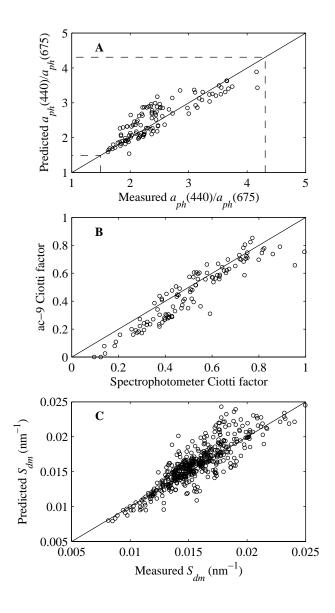


Figure 12.3: Spectral information of the original data was also retrieved by the inversion. (A) The ratio of the phytoplankton absorption maxima, aph(440)/aph(675), from the inversion was significantly related to that from the original  $aph(\lambda)$  when  $aph(440)/anw(440) \ge 0.40$ , r2 = 0.77 N=135. (B) The ciotti factor from the inversion was significantly related to that obtained from the original phytoplankton spectra, same data as in 3A r2 = 0.87. (C) Spectral shapes of non-algal absorption were also retrieved as indicated by the significant relationship between the slope, Sdm, r2 = 0.77 for all data.

Comparison of the ratios of the phytoplankton absorption,  $a_{ph}(440)/a_{ph}(675)$ , and the Ciotti factors,  $f_c$ , retrieved from the inversion with those calculated from the original phytoplankton absorption spectra indicated that spectral variations in  $a_{ph}(\lambda)$  were retrieved with the inversion, Figure 12.3A and B. Similarly, comparison of the spectral slopes of the non-algal absorption from the inversion with those calculated with the original data demonstrated that the inversion retrieved spectral variation of  $a_{dm}(\lambda)$ , Figure 12.3C.

Babin et al. (2003) showed theoretical normalized scattering spectra for both phytoplankton and non-algal particles which varied with particle size and refractive index. Theoretically, scattering shapes for non-algal particles can be described as a power law with slope  $\gamma$  which increases with decreasing particle size. The exponent  $\gamma$  is related to the Junge exponent of the particle size distribution, j, through  $\gamma = j - 3$  (Babin et al. 2003; Boss et al. 2001; Morel 1973). Inclusion of absorbing bands, such as with phytoplankton, is accompanied by decreases in the scattering coefficient. Evidence of the variation in the range of scattering shapes was present in the 25,276 one meter depth-binned ac-9 measurements obtained with the AVPPO deployments prior to 2003 and the 5 minute time-binned data from the cruise EN372 (Fig. 12.4, Morrison and Sosik 2002b). Further analysis demonstrated that greater than 99 % of the variation in the spectral scattering shape could be explained by three normalized scattering spectra, small and large non-algal particles (slopes of 1.63 and -0.20 nm<sup>-1</sup>, respectively) and large phytoplankton. The spectral shape of small phytoplankton was indistinct from the others and was similar to small particles mixed with large phytoplankton.

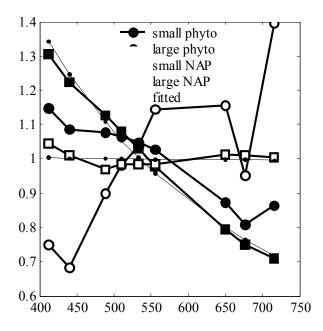


Figure 12.4: The normalized scattering spectra for both small and large phytoplankton and non-algal particles (NAPs) determined from AVPPO ac-9 measurements prior to 2003. Note the troughs in the phytoplankton scattering spectra associated with absorption peaks. The slopes of the fitted values are 1.136 and 0.012 nm-1 for the small and large NAPs, respectively.

### 12.4 CONCLUSIONS

Parameterizing the variability in inherent optical properties associated with optically important constituents is fundamental to understanding variations in ocean color, especially in optically complex regions such as the coastal ocean. Measurements with sufficient resolution, both temporal and spatial, are necessary to encompass the range of possible IOPs and to understand their forcings. Much of this detail has been captured by the Autonomous Vertically Profiling Plankton Observatory during deployments at the FRONT site, in Massachusetts Bay, and at the MVCO. We have explained the majority of the variation in

the measured IOPs by developing models based on characteristic shape vectors. We are currently working to improve ocean color remote sensing inversion algorithms in Case II by including this increased understanding of the natural range of IOPs. This includes approaches utilizing the increased information associated with hyperspectral measurements.

Rigorous use of solar stimulated fluorescence depends on a quantitative understanding the variability of the quantum yield of fluorescence of phytoplankton. Inherent in this is determining the rates of onset and relaxation of non-photochemical quenching. As demonstrated by the data presented herein (Fig. 12.3), the Autonomous Vertically Profiling Plankton Observatory provides an ideal platform for such a study of solar stimulated fluorescence.

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- Morrison, J. R. 2003: In situ determination of the quantum yield of phytoplankton chlorophyll *a* fluorescence: a simple algorithm, observations, and a model. *Limnology and Oceanography* **48:** 618-631.
- Morrison, J. R., and N. B. Nelson. 2003: Seasonal cycle of phytoplankton UV absorption at the Bermuda Atlantic Time-series Study (BATS) site. *Limnology and Oceanography* (in press).

#### Presentations

Morrison, J.R., Sosik, H.M., 2002: Inherent optical properties in New England coastal waters: Decomposition into contributions from optically important constituents. Presented at Ocean Optics XVI, Santa Fe, NM.